

DECONTAMINATION OF METALS CONTAINING PLUTONIUM AND AMERICIUM

by

M. G. Seitz, T. J. Gerding,
and M. J. Steindler



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Chemical Engineering Division

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ABSTRACT

Melt-slagging (melt-refining) techniques were evaluated as a decontamination and consolidation step for metals contaminated with oxides of plutonium and americium. Experiments were performed in which mild steel, stainless steel, and nickel contaminated with oxides of plutonium and americium were melted in the presence of silicate slags of various compositions. The metal products were low in contamination, with the plutonium and americium strongly fractionated to the slags. Partition coefficients (plutonium in slag/plutonium in steel) of 7×10^6 were measured with borosilicate slag and of 3×10^6 with calcium, magnesium silicate slag. Decontamination of metals containing as much as 14 000 ppm plutonium appears to be as efficient as for metals with plutonium levels of 400 ppm.

Staged extraction, that is, a remelting of processed metal with clean slag, results in further decontamination of the metal. The second extraction is effective with either resistance-furnace melting or electric-arc melting.

Slag adhering to the metal ingots and in defects within the ingots is the important contributors to plutonium retained in processed metals. If these sources of plutonium are controlled, the melt-refining process can be used on a large scale to convert highly contaminated metals to homogeneous and compact forms with very low concentrations of plutonium and americium.

A conceptual design of a melt-refining process to decontaminate plutonium- and americium-contaminated metals is described. The process includes single-stage refining of contaminated metals to produce a metal product which would have less than 10 nCi/g of TRU-element contamination. Two plant sizes were considered. The smaller conceptual plant processes 77 kg of metal per 8-h period and may be portable. The larger one processes 140 kg of metal per 8-h period, is stationary, and may be near the maximum size that is practical for a metal decontamination process.

I. INTRODUCTION

Nuclear operations involving work in transuranic (TRU) elements generate large quantities of contaminated waste. Because of the contaminants, the waste is subject to special treatment, as specified in existing or proposed regulations.¹ Metals constitute a large fraction of the volume of such waste and cannot be burned or otherwise treated as can the combustible

material. Furthermore, detection of very low levels of contamination in convoluted metallic forms is not feasible. The purposes of the present study are to demonstrate a method of cleaning contaminated metals and of transforming them into a readily assayed form; both purposes are aimed at more efficient disposal or even recycle of the metals. Prior work on this topic has been reported in earlier reports.^{2,3}

The contaminated metals exist in various forms and with various levels of TRU-element contamination, most of which is plutonium. The metallic waste originated as obsolete equipment and tools and as scrap from operations such as fabrication and processing of nuclear materials. The quantity of material is large and increasing. In one study,⁴ it was estimated that $6.5 \times 10^4 \text{ m}^3$ of contaminated equipment was stored at one facility operated by the U.S. Department of Energy.

Under proposed federal regulations,¹ material that is contaminated with TRU elements in excess of 10 nCi/g cannot be disposed of in commercial burial facilities but must be stored in a retrievable fashion because of their potential hazards.⁵ Costs increase with length of time the retrievable storage facilities are maintained. In any case, retrievable storage is thought of as only a temporary repository for TRU-contaminated metals. Metals may be recycled but proposed federal regulations on TRU content of recycled scrap¹ are more stringent than those for waste destined for disposal. A permanent solution involving decontamination of the metal is required.

A. Previous Work in Metal Decontamination

Decontamination of metallic items contaminated because of service with plutonium or other radioactive elements has been practiced for several reasons. These include for access to and maintenance of equipment in service, for recovery of valuable materials (including plutonium), and for the decommissioning and disposal of obsolete equipment. A significant amount of information is available in the open literature on the subject of decontamination of surfaces contaminated by radioactive materials. In addition to this information, many patents have been issued covering decontamination procedure and materials. A major portion of the available information deals with describing techniques for producing radiation levels low enough for contact work by personnel. The most extensive and detailed literature appropriate to radioactive decontamination of metal surfaces has been provided by workers in reprocessing and reactor operations.⁶ Decontamination and decommissioning of nuclear facilities has also contributed significantly to a phase of decontamination technology characterized by immobilization of radioactive materials, as well as the reduction of activity levels for worker safety and disposal consideration.^{7,8} From these sources much information has come relative to decontamination methods that are successful for reducing beta and gamma activity; however, there is only limited overall information regarding the decontamination of alpha-contaminated materials (particularly those contaminated by plutonium).

The literature is replete with reports detailing processes and techniques for handling transuranic or TRU-contaminated solids and liquids. The bulk of this material addresses procedures for handling liquid effluents, combustible solids, contaminated soil, contaminated laundry, etc., and only a small amount

of this literature deals with the decontamination of TRU-contaminated metals. One review of the literature⁴ covers the application of plutonium decontamination technology to contaminated metals. Another literature review⁹ dealing with the removal of PuO_2 from contaminated metal was prepared in relation to a program for the decontamination of chop-leach cladding hull wastes.

Initial studies using electropolishing as a decontamination technique have indicated that this method is capable of removing beta, gamma, and alpha activity from metal surfaces.^{10,11} The process utilized phosphoric acid electrolyte in producing polished metal surfaces. Another report¹² describes problems associated with increase of plutonium activity levels with time on previously cleaned metal surfaces. The measured alpha activity on a cleaned surface was reported to have increased by a factor of 3.5 after four months. No explanation was given for this phenomenon.

At present there are no chemical cleaners or mechanical methods for decontamination of metallic equipment of moderately complex geometry that can provide assurance by measurements that contamination has been reduced to acceptably low levels. Significant reduction in activity can be obtained by conventional decontamination methods, using solvents and other reagents to transport or dissolve the adhering contamination. Such techniques, applied to readily accessible smooth, metallic surfaces, can be expected to have considerable success. Not amenable to decontamination by solvent and cleaning techniques are (1) inaccessible areas of materials whose surfaces are rough or convoluted and (2) materials that have been subjected to high-temperature service or to corrosive reagents.

Melt refining (melt-slugging) of steels that are contaminated with plutonium has been suggested¹³ as a possible decontamination process which has the potential advantages of producing steel for reuse and simplifying analytical (sampling) problems. Personnel at the Battelle Northwest Laboratories^{9,14,15} and at the Atlantic Richfield Hanford¹⁶ project have carried out melting experiments with metal and have achieved some decontamination. However, the extent of decontamination was not studied because the primary goal of the work was to demonstrate volume reduction and radioactivity immobilization. The National Lead Co. has issued two reports^{17,18} which treat the subject of melt-refining metal scrap contaminated with uranium. The National Lead Co. has continued this study by studying the feasibility of a portable smelter concept.¹⁹ Although acceptable residual contaminant levels for uranium (nonenriched) are significantly greater than those for plutonium-contaminated materials, the developed and proposed techniques for handling uranium-contaminated scrap may be applied, with some modification, to the treatment of plutonium-contaminated scrap.

Results of a laboratory-scale investigation indicated a high degree of decontamination of plutonium- and americium-contaminated metals by pyrochemical methods.²⁰ The use of melting and slagging techniques, using silicate slags and metal to slag weights ratios of about 10 to 1, reduced TRU content from as high as 14 000 ppm in metal to levels of 0.0001-0.001 ppm. These methods are currently under study for application to a large-scale operation.²¹

B. Decontamination of Metal and Conversion to Assayable Form

The isotopes of plutonium and americium are radioactive, generally decaying with emission of alpha particles or gamma rays. In the design of any decontamination process to handle TRU-contaminated metals and to produce a metal product of low contamination, an analytical capability would be required at several stages of the process. Incoming scrap must be surveyed to estimate the fissionable isotope content in order to ensure the absence of fission-sustained chain reactions. The assay of incoming material would also allow highly contaminated metals to be separated from metal of low contamination for more efficient process operation. At high contamination levels, the radionuclides will provide sufficient detectable radiation to readily classify contaminated metals according to activity levels.

In addition, it will be necessary to assay product metals in order to assure that decontamination was effective. These assays would require the detection of TRU elements at contamination levels down to about 10 nCi alpha activity per gram of processed metal. Methods of assaying for TRU elements at low concentrations have been reviewed by Steindler et al.²²

Because of the short range of alpha particles and the rapid attenuation of the beta and gamma rays, nondestructive assays (NDA) for plutonium or americium at low concentrations in convoluted metals of various shapes are difficult to do reliably. It is difficult to assay for low levels of plutonium and americium because the isotopes of an element may be present in any proportions. Therefore, assays for specific isotopes would not indicate the amounts of the elements present. In assaying for plutonium and americium in metal components, there is insufficient ability to detect, with certainty, concentrations, near the limit (10 nCi/g) considered to define transuranic-contaminated wastes.

One solution to this problem would be to form compact and uniform shapes of the metal with a known distribution of plutonium or americium. These shapes could be assayed with external detectors and referenced to standards. Alternatively, the shapes could be sampled, and the samples subjected to detailed analyses.

A method is desired of converting the material to standard homogeneous forms as well as to effect decontamination. Melt-refining techniques were selected to achieve these objectives. These techniques are feasible for the large-scale processing required to handle the quantities of contaminated metals that presently exist or would be expected from future operations.

An experimental program was undertaken to determine the chemical behavior of plutonium in a melt-refining process using different experimental conditions with various metals and slags. The experimental approach and the results of the experiments are described in this report.

Also presented in this report is a conceptual design of a process used to decontaminate metals by melt refining. The design outlines the process steps and considers methods of assaying consolidated and homogeneous forms that would be produced in the process.

II. EXPERIMENTAL TECHNIQUES

For most experiments, steels, plutonium oxide, and slag were loaded into an alumina crucible as depicted in Fig. 1. Metals used in these experiments included a cold-rolled mild steel (analysis: Fe, >99%; C, 0.08-0.23%; P, 0.24%; Si, 0.03%; Mg <0.001% by weight), 304 stainless steel, and nickel-200. Some experiments were performed with mild steel or with mild steel and stainless steel with the addition of minor amounts of copper or brass. The plutonium oxide contained 83.81 wt % plutonium (isotopic composition: ^{238}Pu , 0.050%; ^{239}Pu , 86.46%; ^{240}Pu , 11.84%; ^{241}Pu , 1.48% by weight) and 0.528 wt % ^{241}Am . The specific activity for alpha decay of the plutonium in the plutonium oxide was measured to be 3.28×10^9 d/s per gram of plutonium. The specific activity for alpha decay of the americium in the plutonium oxide was taken to be 1.23×10^{11} d/s per gram of americium, a value that was arrived at by assuming that all the americium was americium-241 that decayed by alpha emission. These specific activities have been used in this work for conversions between radiation counting data and TRU concentrations or between TRU concentrations and alpha activities. The slags used in the experimental work were (1) glasses, (2) industrial slags from steel-making processes, or (3) fused mixtures of metal oxides.

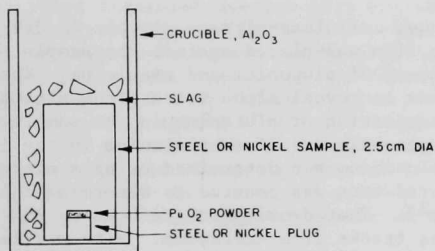


Fig. 1.

Metal and Slag Prior to Melting

As in seen in Fig. 1, the plutonium oxide was retained in a cavity of the steel sample with a metal plug to restrict the accessibility to the slag and to simulate contamination in cracks or embedded on wear surfaces of metals.

Most melt-refining experiments were conducted in a tungsten-mesh resistance furnace (Brew, Model 1064-C) that was capable of providing temperatures as high as 1800°C and any desired atmosphere. The furnace was loaded either with one large crucible (100-mL capacity) containing about 200 g of metal or with three small crucibles (each of 5-mL capacity) containing about 10 g of metal each.

Two other experimental approaches were taken in which the plutonium was in a form different from that depicted in Fig. 1. In one approach, a steel was used that had previously been decontaminated by melt refining but contained

residual plutonium. This approach was used to examine whether staged extraction (i.e., successive melt-refining steps) would produce a cleaner metal product. The other approach was to use plutonium-contaminated slag with clean steel to determine the extent to which plutonium would enter the metal from the slag.

After loading of the furnace, it was evacuated and backfilled with dry helium gas to 53 kPa (400 mm Hg) pressure. The contents of the crucibles were melted by heating to about 1500°C and then maintaining furnace power to keep it at that temperature for 1 or 2 h.

One experiment, experiment 126, was conducted in a small (50-g capacity) arc melter (Centorr, Series 5). Electric power was maintained for 1 min. The solidified slag and metal were easily separated from the water-cooled copper hearth.

Chemical analyses of massive metal (10 g) and slag (50–200 mg) samples were used to determine the average plutonium concentrations in the bulk material. Two additional methods were used to identify the actual association of the plutonium with the metals and slags: One is an autoradiographic technique, sensitive to alpha particles, and used to reveal the microscopic distribution of plutonium and americium in the metals and slags. The technique is adaptable to high or low alpha activities by adjustment of the exposure time. The second method employed is a fission-track analysis technique that records fission particles from neutron-fissioned isotopes. The technique is highly sensitive to plutonium, and there is little interference from the other elements present in these experiments.

In the alpha-radiographic technique, cellulose-nitrate plastic (Kodak Pathe, LR 115, Type II) was used. The film was placed against the sample to register alpha particles from the decay of plutonium and americium. The film was then etched in sodium hydroxide to reveal alpha tracks from plutonium and americium in the sample. The concentration of plutonium in the sample was related to the number of alpha tracks per unit area from plutonium in the sample.²³ The number of tracks from plutonium was determined using a microscope; the number of tracks in a measured area was counted to determine the track density (number of tracks per cm²). That density was reduced by 19% to adjust for the contribution of alpha tracks from americium. With a film exposure of 1 week, the alpha-radiographic technique was determined to be capable of detecting alpha tracks equivalent to about 0.002 ppm ²³⁹Pu in a sample of metal.

In fission-track analysis, the distribution of plutonium was mapped after inducing fission of plutonium and stopping the fission fragments in a solid detector that was in direct contact with the sample. Two detectors were placed between two samples and maintained in position with respect to the samples during irradiation, as depicted in Fig. 2. Sheets of muscovite were used as fission-fragment detectors and were etched in 48% HF (etching was for 12 min at 26°C) after exposure to fission fragments. Each detector registered fission tracks from the sample it was in contact with and was viewed with an optical microscope. The observed distribution of fission tracks revealed the distribution of plutonium within the sample.

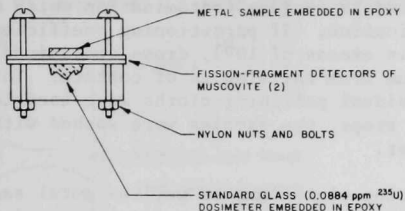


Fig. 2.

Arrangement of Samples and Detectors for Neutron-Activation Analysis

A glass standard containing a known concentration of ²³⁵U was included as a dosimeter sample,²⁴ and plutonium concentrations, C_{Pu}, were determined with the equation:

$$C_{Pu}(\text{ppm}) = \frac{\delta_{\text{sample}}}{\delta_{\text{std}}} \times C_{\text{std}}(\text{ppm}) \times \frac{\sigma_f(\text{U})}{\sigma_f(\text{Pu})}$$

where δ_{sample} and δ_{std} are track densities for the sample and standard glass, respectively, C_{std} is the concentration of ²³⁵U in the standard,²⁵ and $\sigma_f(\text{U})$ and $\sigma_f(\text{Pu})$ are the thermal-neutron fission cross sections for ²³⁵U and the plutonium used in the experiments, respectively [$\sigma_f(\text{U}) = 580$ barns, and $\sigma_f(\text{Pu}) = 660$ barns²⁶].

This treatment assumes that the ratio of effective fission cross sections for uranium and plutonium is equal to the ratio of cross sections for thermal neutrons, an assumption that is not valid if a large fraction of the neutrons from the reactor are nonthermal. Fission of ²⁴¹Am is negligible, being about 2.5×10^{-5} that of plutonium. The treatment also assumes that the ranges (in kg/m²) of fission fragments from ²³⁵U and plutonium in glass and steel are the same; it is known that their agreement is better than 30%. Because measured plutonium concentrations in different samples were compared with each other in evaluating parameters, no effort was made to refine the treatment to reduce any systematic error.

The number of tracks within a specified area was counted to determine the track densities, δ_{sample} and δ_{std} , for the samples and standard glass. When the tracks were uniformly distributed, such as those from the standard glass, an area was selected that gave enough tracks for the statistical accuracy desired.

For inhomogeneous track densities, an area was selected that was representative of the material being measured. This was done by moving the detector under the microscope and counting tracks in several fields of view. Generally, sufficient tracks were counted so that the statistical accuracy was due primarily to inhomogeneities in the plutonium distribution. The statistical accuracy due to the number of tracks counted can be calculated from the counting data.

Because the fission-track method analyzes material at or near the surface of a sample, the method is sensitive to surface contamination which may be present as a result of cross-contamination. If partitioning coefficients between steel and slag are very high (in excess of 10^6), cross contamination of the steel by even traces of plutonium from the slag is of concern. To ensure against cross-contamination, individual polishing cloths were used to prepare each sample; between polishing steps, the samples were washed with distilled water in an ultrasonic cleaner.

Borosilicate glass samples containing plutonium, as well as metal samples, were analyzed by fission-track analyses. Each glass sample was placed in a separate assembly to minimize neutron shielding effects during irradiation (caused by boron in the glass). Only small slivers of glass were irradiated to reduce self-heating and self-shielding effects.

III. EXPERIMENTAL RESULTS

Several crucible materials were tested to determine their ability to contain molten slag and steel. An initial test was performed on each crucible material with CaSiO_3 (mp about 1440°C) as a slag. If the crucible retained the slag, a second test of the crucible was done with CaSiO_3 and steel at 1500°C . For these tests, the metal and slag were allowed to cool and solidify in the crucibles. The materials tested and the results of the tests are presented in Table 1.

Graphite was not subjected to the second test but it is believed it will satisfactorily contain the steel-molten slag material at 1500°C . However, it is effectively a sacrificial material due to its corrosion by molten steel. The introduction of carbon into the steel and slag may affect the chemical behavior of plutonium and americium. Graphite would be considered for crucible material only if no other suitable material is found.

Some success was achieved in the containment of molten steel and slag with crucibles of calcia-stabilized zirconia. However, the crucibles were cracked in each melting test--sometimes after the contents had solidified but most often before the contents had solidified. Cracking of the crucibles before the sample had solidified resulted in loss of the sample.

Recrystallized alumina was found to be superior to the other materials tested. It presented a dense, smooth surface to the steel-slag system, it resisted attack from the molten steel-slag material, and it held up well to the thermal stresses of the furnace system. There were hairline cracks in the crucibles after completion of melting tests;⁵ however, no crucible cracked prior to sample solidification. Because this material contained the slag and steel at high temperatures, it was selected as the containment material for the plutonium-contaminated-steel melting experiments. All subsequent experimental work was done using alumina crucibles.

Table 1. Suitability of Materials as Melt-Refining
Crucible Materials. Tests at 1500°C

Crucible Material	CaSiO ₃ Slag	Steel and CaSiO ₃ Slag
MgO	No	--
Alundum	No	--
"Ruby" ^a	Partially ^b	--
"Guidon" ^a	No	--
"Copur" ^a	No	--
Zircon	Yes	No
Vitrified Carbon	Yes	No
Graphite	Yes	--
ZrO ₂ (CaO-stabilized)	Yes	High frequency of failure
Al ₂ O ₃ (recrystallized) ^c	Yes	Yes

^aThese materials were obtained from the Harbison and Walker Refractories Co. of Dresser Industries, Inc., Pittsburgh, PA.

^bThe crucible material was porous and absorbed the molten slag.

^cThe alumina crucibles type AD-998, were obtained from the Coors Porcelain Co., Denver, CO.

Table 2 lists the conditions for the melt-refining experiments performed with contaminated mild steel, nickel, and stainless steel. In the experiments with mild steel, the amount of slag and its composition were varied to determine the effect on the metal. The metal contamination was held at about 400 ppm Pu by weight for most experiments since this is a typical concentration for scrap, but was increased to about 14 000 ppm Pu in experiments 121 and 124 to determine the effects of higher levels of plutonium on the melt-refining process.

Table 2. Experimental Conditions for Melt-Refining Contaminated Metals
(Reaction temperature, about 1500°C; Helium cover gas at
5.3 x 10⁴ Pa)

Exp. No.	Metal	Metal Wt, g	Pu Wt, mg	Initial Steel Contamination, ppm Pu	Slag Material	Slag Wt, g	Slag/Metal Wt Ratio	Time at Temp, h
53	Steel	204	82	400	none	none	—	1
73	Steel	204	92	450	CaSiO ₃	10.0	0.05	1
76	Steel	197	83	420	CaSiO ₃	22.5	0.11	1
78	Steel	203	82	400	CaSiO ₃	41.7	0.20	1
80	Steel	205	87	420	Borosilicate ^b	20.4	0.10	1
82	Steel	206	89	430	Borosilicate	39.9	0.19	1
101	Steel	206	83	400	CaMgSi ₂ O ₆	20.0	0.10	1
103	Steel	205	93	450	Ca-Al Silicate ^c	20.1	0.10	1
105	Steel	205	83	400	Hearth Slag ^d	20.7	0.10	1
107	Steel	205	83	400	Ca-Al Silicate	20.1	0.10	2
109	Steel	209	85	410	Borosilicate	20.1	0.10	2
111	Steel	203	87	430	Borosilicate	40.0	0.20	2
113	Steel	240	0.03 ^e	about 0.1	Borosilicate	20.1	0.08	1
115	Steel	207	59	280	Borosilicate	19.9	0.10	1
117	Nickel 200	222	82	370	Borosilicate	20.2	0.09	1
119	Stainless Steel 304	191	85	445	Borosilicate	19.9	0.10	1
121-1	Steel	12.2	5.0	410	Borosilicate	1.29	0.10	1
121-2	Steel	11.4	99.7	8 750	Borosilicate	1.31	0.12	1
121-3	Steel	12.0	165	13 700	Borosilicate	1.27	0.11	1
124-1	Steel	11.8	7.8	660	CaMgSi ₂ O ₆	2.20	0.19	1
124-2	Steel	13.1	93	7 100	CaMgSi ₂ O ₆	1.94	0.15	1
124-3	Steel	13.2	188	14 300	CaMgSi ₂ O ₆	1.96	0.15	1
126 ^f	Steel	—	—	0.004	Borosilicate	—	—	0.02
129	Steel, 4 wt % Copper	216.8	85	410	Borosilicate	20.2	0.10	1
130-1	Steel	201	85	424	Borosilicate	20.0	0.10	1
130-2	Steel	204	89	434	Borosilicate	20.2	0.10	1
133	Turnings	40.5	—	—	Borosilicate	4.2	0.11	1
135	Steel, 4 wt % Copper	214	86	400	Borosilicate	20.0	0.093	1
137	Steel, 45 wt % Stainless Steel 304	188	80	430	Borosilicate	20.1	0.107	1
139	Steel, 45 wt % Stainless Steel 304	195	84	430	Borosilicate	20.2	0.104	1
141	Steel, 45 wt % Stainless Steel 304, 9 wt % brass	185	85	460	Borosilicate	20.2	0.109	1
145	Nickel	200	104	520	Borosilicate	20.1	0.100	1

^a"Steel" in this column represents mild steel.

^bNominal composition of the borosilicate glass is 81.0% SiO₂, 13.0% B₂O₃, 4.0% Na₂O, 2.0% Al₂O₃, and 0.5% K₂O by weight. The glass was number 7740 from the Dow Corning Corporation.

^cCa-Al Silicate is a commercial blast furnace slag containing minor amounts of Mg, Ti, V, Mn, and possibly Fe as determined by microprobe analysis. Gehlenite crystal (Ca₂Al₂SiO₇) and some ackermanite (Ca₂MgSi₂O₇) were detected by X-ray diffraction.

^dHearth slag is a commercial open hearth furnace slag containing CaFeSiO₄ melilite (solid solution of gehlenite and ackermanite) with a minor amount of α-SiO₂ as determined by X-ray diffraction.

^eSteel from experiments 80 and 82 was used in staged-extraction experiment 113. The plutonium concentration was calculated from measured plutonium concentrations of these samples.

^fThe slag and steel were melted in a copper hearth in an electric-arc furnace. Staged extraction.

After melting and solidification in the resistance furnace, the relationship of the metal to slag was as depicted in Fig. 3.

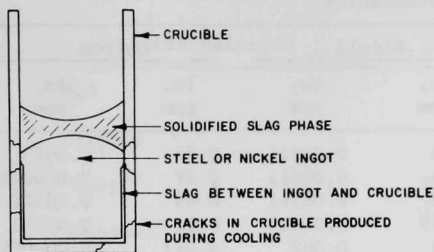


Fig. 3.

Crucible and Contents after Melting and Resolidification

Many of the crucibles cracked, probably during cooling, due to differential thermal contraction of the crucible, metal, and slag. The metal ingots had shiny surfaces, varying from smooth to pitted; generally, fragments of slag adhered to them. Each metal ingot was cut into five sections, as shown in Fig. 4.

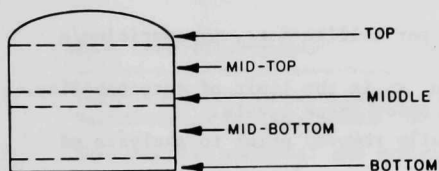


Fig. 4.

Ingot Sectioning Diagram

A. Metal Analyses

1. Chemical Dissolution and Radiochemical Counting

Analyses of top, middle, and bottom samples for plutonium and americium were done by chemical dissolution and radiochemical counting. The results are given in Table 3.

The analyses indicate extensive fractionation of the plutonium to the slag. Some of the metal samples had plutonium concentrations below the 10-nCi/g (about <0.1 ppm plutonium) level currently used to define TRU-contaminated wastes. The low plutonium levels (Table 3) were achieved without special treatments to separate slag from metal (such as trimming or electropolishing the surface of the ingot). Generally, the center sections of the ingots had lower plutonium and americium concentrations than did the tops or bottoms, suggesting that significant fractions of the residual plutonium and americium were associated with the surface of the ingots.

Table 3. Plutonium and Americium Concentrations in Samples of Melt-Refined Steel. Analyses by aqueous dissolution and radiochemical determination

Exp. No.	Top		Middle		Bottom	
	Pu, ^a ppm	Am, ^b ppm	Pu, ppm	Am, ppm	Pu, ppm	Am, ppm
53	Very High	Very High	1.03	0.00015	0.77	0.0053
73	6.4	0.049	0.54	0.00011	0.27	0.000048
76	22.0	0.150	0.26	0.00161	0.09	0.00045
78	7.56	0.076	0.065	0.00035	0.12	0.00093
80	0.029	<0.000038	0.22	0.002	0.017	0.000025
82	0.060	0.000001	0.041	<0.000001	0.32	0.0018
101	21.0	0.100	0.18	0.00018	0.69	0.0018
107	1.6	0.200	0.10	0.00026	0.09	0.00027
109	0.002	<0.000001	0.0012	<0.000001	0.003	<0.000001
111	0.005	<0.000002	0.0096	<0.00005	0.20	0.000025
113	0.002	<0.000001	0.0011	<0.000001	0.002	<0.000001
115	0.002	<0.000001	0.03	<0.000001	0.006	<0.000001
130-2 ^d	0.00009	<0.000001	0.00007	<0.000001	0.00007	<0.000001

^aPlutonium concentrations are in parts per million (ppm) i.e., μg plutonium/g steel after melting.

^bAmericium concentrations are in parts per million i.e., μg americium/g steel after melting.

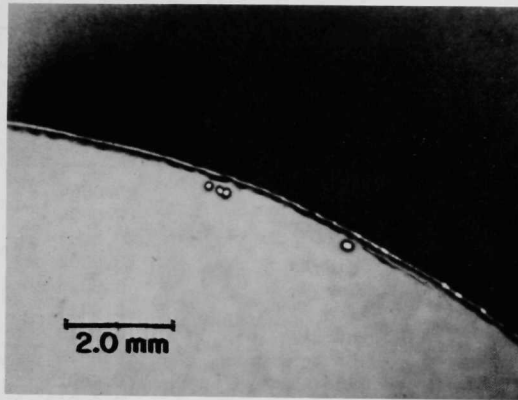
^cA value following the "less than" sign, <, is the limit of detectability. The concentrations in the metals were below these levels.

^dThe surface of the ingot was mechanically removed prior to analysis of this ingot.

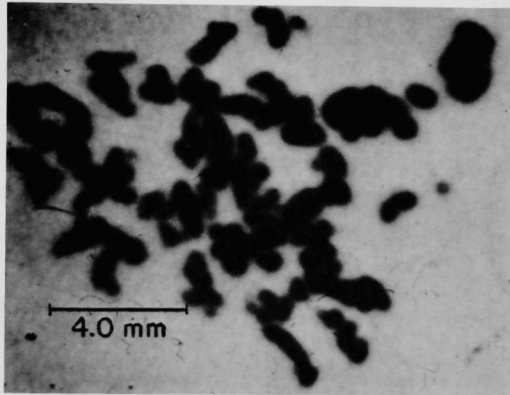
2. Alpha Radiography

Alpha-radiographs were made from metal samples cut from the ingots. The radiographs indicate that the alpha activity was predominantly on the surface of the ingots. All ingots analyzed showed this effect. Plutonium, as determined from the radiographs, also occurred in the interior of some ingots; where present in concentrated form, plutonium was associated with visible defects (not all visible defects in the metals had plutonium associated with them however). Photomicrographs showing alpha activity at the surface of the ingot and at visible defects are given in Fig. 5. Occurrences of plutonium at the metal surface or in visible defects accounted for most (>99%) of plutonium associated with the metal. Only occasionally did a point source of high alpha activity appear in an area of the steel where there was no observable defect. The alpha activity, in these cases, may have been due to a defect immediately below the cut surface.

With the exceptions given above, large areas of the interior of the steel were found to be very low in alpha activity. Exposure to radiographic film for several days resulted in no alpha tracks from the interior of some samples. Hence, the plutonium concentration determined from alpha radiographs



(a)



(b)

Fig. 5. Alpha Radiographs of Samples from Steel Ingots. Alpha tracks appear dark in transmitted light. (a) Alpha activity from inclusions at the ingot surface can be seen at the upper right with low activity from the metal at the lower left. The scratch is a fiducial mark approximately at the ingot surface. (b) Region of high alpha activity from visible defects within ingot. ANL Neg. No. 308-77-325

Table 4. Plutonium in Metal Samples.
Analyses by Alpha Radio-
graphy

Exp. No.	Sample	Conc. Pu, ppm
53	Mid-Top	<0.0004
73	Mid-Top	<0.0004
76	Mid-Top	<0.0004
80	Mid-Top	<0.0005
82	Mid-Top	<0.0004
101	Top	0.0016
107	Top	0.0018
	Middle	0.0010
	Bottom	0.0010
109	Top	0.00019
	Middle	0.00019
	Bottom	0.00017
111	Top	0.0018
	Middle	0.0016
	Mid-Bottom	0.0029
113	Top	0.00001
	Middle	0.00003
	Bottom	0.000009
115	Top	0.00003
	Middle	0.000004
	Bottom	0.00008
117	Top	0.0293
	Bottom	0.0438
119	Top	0.0030
121-1	Average ^a	0.0060
121-2	Average	0.0063
121-3	Average	0.0186
124-1	Average	0.0037
124-2	Average	0.0162
126	Average	0.0012
129	Mid-Top	0.0637
130-1	Top	0.0003
130-2	Top	0.0002
133	Average	0.0010
135	Top	0.0004
	Middle	0.00019
	Bottom	0.00022

(contd)

With the exceptions given above, large areas of the interior of the steel were found to be very low in alpha activity. Exposure to radiographic film for several days resulted in no alpha tracks from the interior of some samples. Hence, the plutonium concentrations determined from alpha radiographs of the metal samples given in Table 4 are only upper limits for plutonium in the matrix of the metal (exclusive of silicate inclusions or other visible

Table 4. (contd)

Exp. No.	Sample	Conc. Pu, ppm
137	Top	0.0015
	Mid-Top	0.0012
139	Top	0.0014
	Mid-Top	0.0011
141	Top	0.0005
	Mid-Top	0.0004
143	Top	0.0007
	Mid-Top	0.0005
145	Top	0.032
	Mid-Top	0.103

^aMeasurements of average plutonium were made by counting alpha tracks from a vertical surface cut from top to bottom through the ingots.

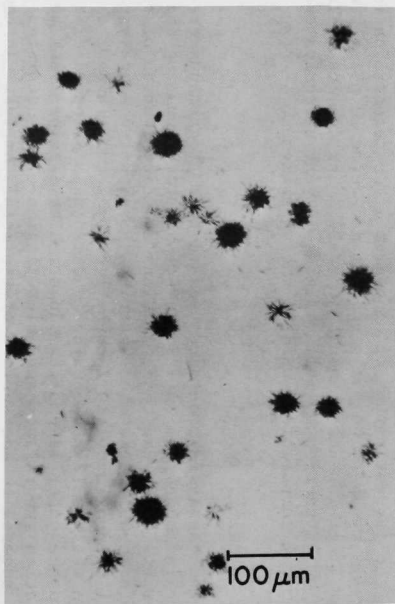
defects). The track-counting data used to determine the plutonium concentrations of the metal from the alpha radiographs are given in Table A-1 of the Appendix.

Except for the nickel samples (experiments 117 and 145), all metal samples generally have concentrations below 0.010 ppm plutonium; for some samples, concentrations are well below 0.001 ppm.

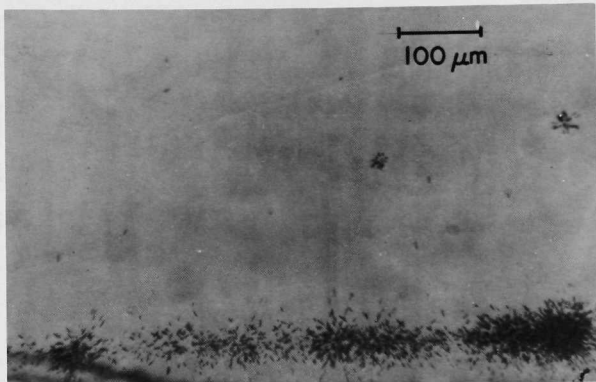
It appears that the addition of minor amounts of copper or brass to mild steel or mild steel plus stainless steel (experiments 129, 135, and 141) did not prevent the effective extraction of the plutonium from the metal. The nickel metal contained the largest amount of plutonium after decontamination. However, even these levels of up to 60 ppm plutonium are below 10 nCi/g (considered to be the upper limit for uncontaminated metal). The results in Table 4 indicate that plutonium extraction by melt refining is very effective over the range of slag and metal compositions used in the experiments.

3. Fission Track Analysis

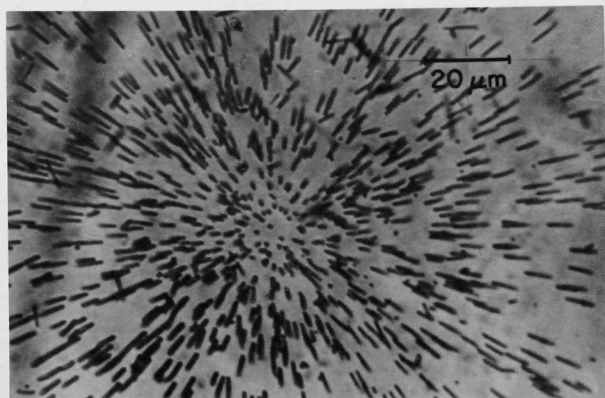
The fission-track analysis procedure used in this program has greater sensitivity than either radiochemical analyses or alpha-track counting and was particularly useful for examining the concentrations and distribution of plutonium at the low levels found in the steel matrix. Fission-track analyses were performed on small (approximately 0.2 cm by 1 cm by 2 cm) slabs of the metals. A metal sample was usually taken along the radius and included material from the center to the outer edge of the ingot. The fission-track maps made by neutron irradiation generally showed high fission-track densities from tiny bits of slag that adhered to the surface of the metal samples. In comparison, relatively few fission tracks were generated in the bulk steel. The tracks generated in the steel were clustered, indicative of localized concentrations of plutonium.



(a)



(b)



(c)

6. Fission Tracks in Mica from Pu in Metal Samples. (a) Track clusters from plutonium in metal corresponding to about 0.01 ppm Pu, experiment 111. (b) High plutonium concentration along edge of metal ingot (bottom, left to right); few tracks from metal matrix (upper) corresponding to about 0.0005 ppm Pu, experiment 109. (c) High-magnification of typical track cluster, showing individual tracks from plutonium fission.

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Photomicrographs showing fission tracks from plutonium associated with metal ingots are presented in Fig. 6. The types of plutonium associations with metal ingots, seen from alpha radiographs and from fission-track analyses are depicted in Fig. 7.

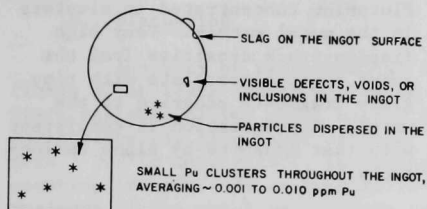


Fig. 7

Types of Plutonium Associations Identified in Melt-Refined Metal

The sizes of particles occurring near the metal surface were calculated from the number of tracks in a star-like pattern, using the neutron-fission cross section and the measured neutron fluence. The dispersed plutonium particles each typically contained about $>2 \times 10^9$ atoms plutonium, and the clusters of plutonium throughout the metal matrix contained less than about 2×10^8 atoms of plutonium per cluster; the smallest detectable size was about 8×10^5 atoms per cluster. However, differences were seen in samples from different experiments (e.g., clusters in metal from experiment 109 varied from the lower limit to about 1×10^6 and in experiment 111 they varied from the lower limit to about 8×10^6 atoms per cluster).

In Table 5, the plutonium concentrations determined by fission-track analyses are given. The concentrations were determined from the data given in Table A-2 (Appendix) and are consistent with the very low concentrations of plutonium determined for the same samples by alpha radiography. This consistency indicates that there is no measurable chemical fractionation of plutonium and americium during melt refining in these samples. Therefore, americium concentrations can be determined for these samples by assuming a constant proportion of americium to plutonium and multiplying the elemental plutonium concentration by 0.0063.

The cause of the variations in plutonium concentration in metals from different experiments is not apparent. For example, the plutonium level in metal from experiment 109 is lower by about a factor of 10 than in metal from experiment 111. These experiments were performed with similar weights of steel and plutonium, but the weight of slag in experiment 109 was half that in experiment 111 (20 g vs. 40 g). The metal from experiment 111 would therefore be expected to have a lower plutonium concentration assuming there is a constant partitioning ratio between slag and steel. The observed behavior may be due to the partitioning coefficient being sensitive to experimental parameters such as temperature or trace impurities. In any case, it appears on the basis of the experimental results that increasing the slag to metal weight ratio does not necessarily result in improved decontamination of the metal.

Table 5. Analyses of Metal Samples by Fission-Track Analyses

Exp.	Sample	Pu, ppm	Comment
101	Mid-Top	0.0018	Plutonium concentrated in clusters in the metal matrix. Very high fission-track densities from the ingot surface correlate with tiny glass fragments adhering to the metal. Concentration is consistent with that measured by alpha radiography.
107	Top	---	Track density in clusters was too high to resolve. An accurate plutonium concentration is measured by alpha radiography.
109	Top	0.0005	Plutonium is in resolvable clusters.
111	Top	---	Track density in clusters was too high to resolve. The estimates of plutonium concentration by alpha radiography were relied on.
113	Staged extraction--both extractions performed using borosilicate glass. Top of the ingot, center to edge.	0.0001	Plutonium in metal matrix is clustered. The second extraction effectively lowered the plutonium content in the metal.
115	Back extraction, plutonium was added via the slag (borosilicate) to uncontaminated metal. Top of ingot (Fig. 4), center to edge.	0.0005	Plutonium in metal matrix is clustered. Plutonium entered the metal from the slag.
	Top of ingot (Fig.4).	0.0004	
126	Low Pu-bearing metal (0.01 ppm) vertical cross section through center of ingot.	0.00004	Background of 0.00003 ppm was subtracted. The few fission tracks indicate that the plutonium in the metal is not clustered.
Blank	Uncontaminated	<0.00001	Fission tracks not attributable to the background of 0.00001 ppm plutonium from the mica were detected.

From the fission-track maps of the metal that was arc melted in experiment 126, the plutonium was found to be uniformly distributed rather than in small clusters as seen in other metals. The reason may be that the arc-melted metal cooled more rapidly than did metal melted in the resistance furnace, allowing insufficient time for precipitates of plutonium to grow during cooling.

4. Discussion

Analyses by radiochemical counting of solutions of metal samples (Table 3) indicate higher plutonium concentrations than do alpha and fission-track analyses of the metal matrix because the former include plutonium from the surface and from ingot defects, as well as plutonium from the metal matrix. Due to this effect, the plutonium content determined by radiochemical counting is sometimes as much as 10^4 times greater than autoradiographic analyses of the metal matrix (see samples 73, 76, 78, 80, 82, 101, and 107).

Some samples were found to have low plutonium contents both by radiochemical counting and by radiographic techniques, which indicates that the samples did not have plutonium-containing defects and had few surface inclusions. This is the case for some samples from experiments 80 and 82 and for all samples from experiments 109, 111, 113, and 115.

B. Slag and Crucible Analyses

After melting and solidification in the melt-refining process the slag adhered to the crucible and had to be fractured to obtain pure samples for dissolution and radiochemical counting. Analyses of slag samples of from 50 to 200 mg in size are given in Table 6.

The total quantity of plutonium in a slag (Table 6) was calculated from the measured concentration of plutonium in the slag by assuming that no weight change of the slag occurred in the melt-refining procedure and that the analyzed slag samples are representative of the entire slag. Total plutonium, expressed as the percentage of the initial amount added to the metal, is also given in Table 6. Because most of the plutonium is removed from the metal during melt refining and because it was found by analyses that crucibles are not a reservoir for plutonium, most of the plutonium used in the experiments would be expected to be in the slags. The range of values exhibited (from <1% to 220% of total plutonium) suggests that either the analyses or the assumptions used to estimate the total plutonium were in error.

Radiographs from alpha radiography and from fission-track analyses were used to determine the distribution of plutonium in slag and crucible samples. The radiographs indicate that plutonium concentrations were high as expected. Inhomogeneities of plutonium distribution in most slags were noted. For example, the alpha radiograph of the sectioned ingot and slag from experiment 121-3 (the slag sample having the lowest percent of the initial plutonium, Table 6) revealed that most of the plutonium was associated with slag on the lower surface of the ingot. In comparison to the quantity of plutonium in the slag on the lower surface, little plutonium was associated with the slag on the top surface of the ingot, where the sample for radiochemical counting had been obtained. Thus, nonhomogeneous distribution of plutonium in the slag accounts for the low percentage of plutonium calculated from the analyses.

Table 6. Analysis of Slags by Aqueous Dissolution and Radiochemical Counting. Types of slags are listed in Table 2.

Exp.	Actinide Conc.		Total Pu in Slag, mg	Pu in Slag, % of Initial Pu
	Pu, mg/g	Am, ppm		
73	4.7	27.3	48	52
76	2.7	24.4	61	74
78	2.1	15.8	86	105
80	4.0	26.0	83	95
82	2.0	17.6	78	88
101	4.8	41.6	96	115
105	1.5	13.2	31	37
107	1.9	16.9	38	46
109	9.3	71.4	187	220
111	0.83	6.7	33	38
113	0.10	0.7	2	a
115	2.3	19.0	46	78
117	2.9	27.1	59	72
119	3.0	27.2	60	71
121-1	1.0	8.1	1	24
121-2	2.4	18.6	3	3
121-3	1.1	10.0	1	0.8 ^b
124-1	2.5	19.1	6	71
124-2	27	200	52	56
124-3	37	330	73	39
129	6.5	48.4	131	155
130-1	7.4	55.8	148	145
130-2	6.6	47.8	133	125

^aInitial plutonium concentration not accurately known.

^bAutoradiographic analysis of this slag indicated that the slag phase is not homogeneous.

The large variation of percent of the initial plutonium in the slag (Table 6) is attributed to inhomogeneities of plutonium distribution. Results of analyzing some slags by alpha radiography and fission tracks are listed along with comments in Table 7.

An attempt was made to correlate track clusters observed in the mica with visible features of the polished metal mounts. This was done by photographing corresponding areas of the mica and steel, tracing major features of the photos on transparent plastic, and superimposing the plastic on the corresponding photograph. Although microscopic features of the steel such as grain boundaries and distinct mineral phases were visible on the photograph, no correlation was evident between the track clusters and features of the steels.

After melting and solidification in the crucible the slag was often a translucent glass of uniform coloration. Slag fragments of uniformly blue glass contained homogeneous distributions of plutonium. Some experiments in

Table 7. Plutonium in Slags Determined by Alpha Radiography and Fission Track Analysis
Original slag compositions are given in Table 2.

Exp. No.	Sample	Results and Comments
107 ^a	Slag, light- and dark-colored	Uniform concentrations of plutonium throughout slag. No difference in the major-element chemistry of the light- and dark-colored slag was detected. ^b
113 ^a	Slag	Plutonium concentrations correlate with the blue-grey portions of marble-colored glass. About 160 ppm average plutonium concentration in glass.
115 ^a	Slag	Dark-colored clear glass in the vicinity of the metal with opaque glass further distant. Both layers show uniform, high concentrations of plutonium, about 2 000 ppm. Slag that was near the crucible contains strips low in plutonium that may be crucible material that was undercut from the wall. A small amount of floating material on the top edge of the opaque glass is higher in alpha activity than is the opaque glass, but represents only a minute fraction of the total alpha activity of the slag (<0.1%).
119 ^a	Slag, different colorations	High plutonium concentrations in the alumina-rich, silica-deficient phase. Low plutonium concentrations in the alumina-deficient, silica-rich phase. ^b
121-3 ^a	Slag, adhering to the metal ingot	Very high plutonium concentrations in the slag that was near the ingot. Relatively little plutonium in the major mass of slag above the ingot.
126 ^c	Borosilicate slag from arc-melting	Plutonium concentrations were high (0.09 ppm) in the slag adjacent to the metal, and diminished to about 0.00003 ppm at a distance from the metal. Plutonium concentration in the slag averaged 0.0098 ppm.

^aAnalyses by alpha radiography.

^bMajor element chemistry determined with electron microprobe.

^cStaged extraction analyses by fission track analysis.

which borosilicate glass was used (113 and 115) generated slags with marbled coloration for which different colors corresponded to variations in the concentrations of plutonium. However, although the slag from experiment 107 contained two materials of distinctly different colors, the plutonium distribution was uniform. This slag was found by electron microprobe examination to have uniform major-element concentrations as well. The slag from experiment 107 (originally commercial, blast furnace slag) was found to be a calcium-aluminum silicate with minor constituents of Mg, Ti, V, and Mn. No variations in major or minor element composition were detectable within the slag, including regions of different coloration. It is concluded that the slag was homogeneous in composition and consisted of a single liquid phase having a uniform plutonium distribution.

The slag from experiment 119 (with borosilicate glass and stainless steel) was found to consist of two phases having different chemical compositions; different-colored areas had different plutonium concentrations. The phase having a high concentration of plutonium is high in alumina and low in silica in comparison to the phase having a low plutonium concentration. The high-plutonium phase also has detectable quantities of potassium and sodium, which are absent from the low-plutonium phase. Small amounts of iron and chromium, presumably from the stainless steel, are found in both phases, with chromium concentration being higher in the alumina-rich phase. The energy spectra of X-rays from electron excitation of the two phases are shown in Fig. 8. Boron, a major constituent of the glass, is not detectable with the electron microprobe.

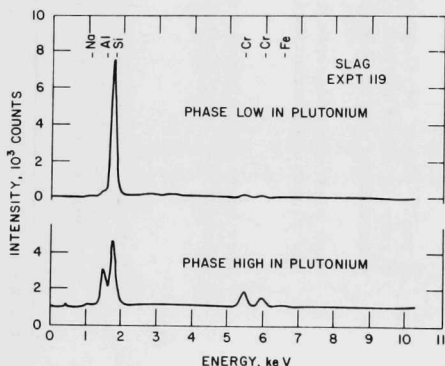


Fig. 8

X-ray Spectra of Slag Phases. Borosilicate Glass-Stainless Steel 304. Experiment 119.

These two phases may originate from a homogeneous glass as a result of the formation of two immiscible liquids such as occurs, for example, in the sodium borosilicate system;²⁷ in the more complex system employed here, high-silica and high-alumina phases may form upon cooling. During the formation of the two phases, plutonium (along with the alkali metals, sodium and potassium) remained almost entirely with the phase high in alumina. This suggests that plutonium, as well as other large ions as defined by Goldschmidt,²⁸ may be more compatible with a slag that is low in silica than with the borosilicate glass used in these experiments.

Zones of reaction between slags and crucibles were observed visually in cross section and were analyzed by alpha radiography. Thin layers of slag, rich in plutonium, were found between the sides and bottoms of the ingots and the crucibles. In the reaction zone (the narrow band of slag between the metal and crucible), the plutonium concentration was seen to diminish near the crucible. Parallel to the crucible, slivers (presumably crucible material that was undercut and floated off the crucible wall) were occasionally seen which were free of plutonium. Reaction of slag with crucible material may limit the service of crucibles in a melt-refining process. Not investigated in these experiments was the selection of slag and crucible materials that would reduce the degradation of crucibles.

C. Staged-Extraction Experiments

Experiment 113 was performed with clean borosilicate glass and with steel that had been melt refined in previous experiments (80 and 82). In experiment 113, approximately equal amounts of steel from experiments 80 and 82 were used. The steel used was taken from the middle sections of the ingots, whose analyses are given in Table 3. After melting, the slag was found to contain 160 ppm plutonium (Table 7), a result that is significantly different from the value of 1.5 ppm calculated on the basis of the plutonium concentrations in the steel obtained by radiochemical analysis. The unexpectedly high plutonium concentration observed in the slag may have resulted from undetected inclusions, rich in plutonium, in the process steel (the total amount of plutonium in inclusions would have had to equal 5% of the total plutonium used in either experiment 80 or experiment 82). An improbable source of plutonium is slag from previous experiments adhering to the steel surfaces since the amount of slag that would be required to account for the experimental results would have been easily visible (approximately 1 g of slag from experiment 80 or 2 g of slag from experiment 82).

The results of experiment 113 do, however, indicate a significant benefit from staged extraction. Plutonium was concentrated in the slag, suggesting that a strong partitioning of plutonium to the slag occurred, with resulting decontamination of the steel. Low concentrations of plutonium in the bulk samples of steel (Table 3) point to staged extraction as being an efficient decontamination step.

Staged extraction by arc melting was conducted (experiment 126), using processed metal from experiment 111 containing 0.003 ppm plutonium. Analyses indicate a significant reduction in plutonium content of the metal (Tables 4 and 5) and an increased plutonium content of the slag (Table 7).

IV. GENERAL DISCUSSION OF EXPERIMENTAL RESULTS

Incomplete separation of silicate slag from steel is the major source of the activity remaining with the ingots. Defects visible on cut surfaces of the ingots often have plutonium associated with them. Although defects are

not abundant, they are the sites of the second largest occurrence of plutonium in the processed metals. A small amount of plutonium occurs throughout the ingot in the form of tiny clusters (from about $>10^5$ to about 10^6 atoms/cluster) that generally constitute very low concentrations (0.001 - 0.010 ppm) of the plutonium in the processed metals. These results indicate that a high degree of decontamination can be obtained by limiting (1) the amount of slag carried with the steel and (2) the formation of internal defects in the ingot.

Plutonium throughout the ingot in the form of small clusters may be precipitated when the metal ingot slowly cools. This is suggested by their uniform spacing and size, which would occur if precipitates formed during uniform cooling of the ingots. In addition, the processed nickel metal contains a larger concentration of plutonium which occurs in clusters than does mild steel or stainless-steel metals; this suggests that the concentration of plutonium in the metal is chemically controlled (rather than being controlled by the particle size of the plutonium oxide powder) and that the plutonium is more soluble in nickel than in the steels. Because of the finite solubility of plutonium oxide in metal, any small quantity of plutonium in scrap metal would be dissolved and dispersed in the steel, generating a metal of uniform composition for assaying.

Apparent partitioning coefficients, K_D , of plutonium between silicate slag and metal [(concentration in slag) \div (concentration in metal)] were calculated. For experiments with small amounts of plutonium (400 ppm) introduced, partitioning coefficients were 2×10^6 to 8×10^6 for mild steel and stainless steel and about 5×10^4 for nickel. In Fig. 9, plutonium concentration in slag after melt refining is plotted against concentration in the process metal for experiments in which the plutonium loading was varied.

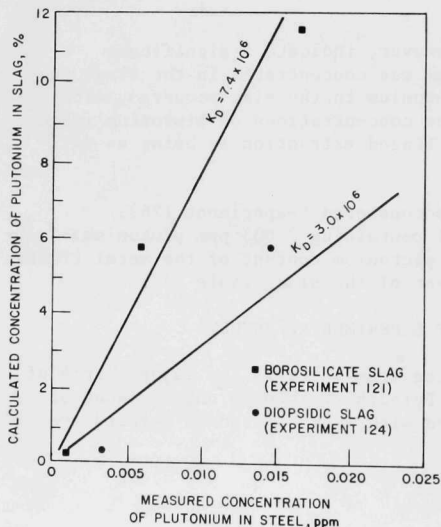


Fig. 9.

Plutonium Concentrations in Slag
vs. Plutonium in Metal

The graph indicates efficient extraction of plutonium from scrap metal with an initial loading in the metal of up to about 14 000 ppm plutonium. The melt-refining process does not appear to be overly sensitive to the chemistry of the slag since similar extractive behavior of plutonium was observed for a range of silicate slag compositions. The difference in the extraction of plutonium from metals by different slags as seen in Fig. 9 would not lead to a significant difference in decontamination because with either slag, residual plutonium levels are low compared with the 10-nCi/g limit used to define TRU-contaminated metal.

In all experiments, the plutonium was strongly fractionated into the silicate phase. Although differences were noted in slag appearance, ease of separation from the ingot, etc., there were few indications that one slag composition was better than another.

The chemistry of the various slags had some effect on plutonium extraction. As noted previously, the data plotted in Fig. 9 indicate that the slag of borosilicate glass extracts plutonium from metal to a greater extent than does diopsidic slag. Also, a slag (originally borosilicate glass, experiment 119) showed two distinct chemical phases as well as large variations in plutonium concentration after use in melt refining. The phase that was low in silica was high in plutonium. This suggests that a slag with a lower silica content (less than the 81 wt % in the borosilicate glass) would extract plutonium better than does slag of borosilicate composition.

V. CONCLUSIONS FROM THE EXPERIMENTAL PROGRAM

In the experimental effort, the melting-slugging process was evaluated as a decontamination step. The process was tested with mild steel, nickel, stainless steel, and mild steel with a trace of copper. The results indicate that plutonium fractionates very strongly into a silicate liquid in preference to the molten metal. For example, for mild steel, more than 99.9% of the plutonium is extracted from the steel and is retained by the slag. Decontamination of metals containing as much as 14 000 ppm plutonium appears to be as efficient as for metals with plutonium levels of 400 ppm. Silicate slags of different chemical compositions were found to efficiently decontaminate plutonium-contaminated metals. Results of the experimental program indicate that staged extraction--that is, recycling processed steel through the melt-refining process is an effective procedure for reducing the plutonium level of the product metal. The second extraction may be done effectively by either resistance-furnace melting or arc-melting. Slag adhering to metal ingots and defects in ingots are important contributors to plutonium retention in process metals. With these sources of plutonium retention controlled, the melt-refining process can be used on a large scale to convert highly contaminated metals to homogeneous and compact forms suitable for assaying and containing very low residual concentrations of plutonium.

VI. CONCEPTUAL DESIGN OF PYROREFINING PLANT FOR DECONTAMINATION OF TRU-CONTAMINATED METALS

A. Introduction

The laboratory-scale, experimental program revealed the potential of melt refining to effectively decontaminate TRU-contaminated ferrous and nickel metals for low-level disposal or possibly recycling. A conceptual design of a refining plant using laboratory-tested melt-slugging techniques was formulated to assist in the planning for an operating plant. The conceptual design includes a significant scale-up factor over laboratory operations and incorporates some operating procedures which appeared advantageous based on experience gained from the experimental program but which have not been tested.

The conceptual design is described in three parts. First, the types and compositions of input material, the capacity of the process, and the characteristics of the output products, all of which constitute the design criteria, are specified. Next, the process steps that a batch of material would undergo in the transformation to the final products are described. Finally, considerations extraneous to the process itself but important to the operation of a plant are outlined.

B. Design Criteria

1. Input Materials for Processing

For design criteria, metals, predominantly steels, having about 400 ppm TRU-contamination were assumed to be the typical materials to be processed in the plant. In items such as machinery or process equipment having high contamination levels (>400 ppm) some of the TRU elements would be likely to be present as dust in crevices or scale in pipes. These concentrations could be removed prior to melt refining to reduce the contamination level of the metal.

If metals with contamination levels of 400 ppm or lower should be processed, slags of low TRU content would be obtained which could be reused. Reuse of slag would result in continued concentration of plutonium and americium and would reduce the mass of contaminated material in the waste stream. In the design of the conceptual process it would be desirable to provide for this reuse without additional process steps.

The melt-refining process is not restricted to materials of about 400 ppm TRU content. For example, if the slag could be recycled, essentially uncontaminated metals suspected of contamination could be processed without producing waste proportionate to the quantity of processed metal. Also, in

the experimental program, metals containing up to 14 000 ppm (1.4 wt %) plutonium contamination were effectively decontaminated by melt refining. This level may be in excess of that permitted by other considerations. For example, given the large batch sizes envisioned for the process plant, restrictions to eliminate the possibility of a criticality event may limit the metals processed to those containing far less than 14 000 ppm feasible for decontamination by melt refining.

It is assumed that the metals are not contaminated with beta-gamma emitting nuclides that would limit or prohibit close access of operating personnel to the materials.

The metals to be melt refined are considered to be predominantly steels (ferrous metals or stainless steels) or nickel, possibly containing minor amounts of other metals such as copper or brass. In the experimental program, it was found that the presence of up to 5 wt % copper in mild steel did not have a detrimental effect on the decontamination process. Similarly, brass at these levels was found to be not detrimental to the decontamination of steels. This behavior may be considered to exist for all ferrous and nickel metals containing less than 5% copper or brass.

The effect of adding minor amounts of metals other than copper or brass is uncertain. For example, lead or lead-tin alloys, which may not affect the chemical extraction of plutonium or americium from metals, may volatilize and interfere with off-gas treatments at the temperatures required to melt ferrous or nickel metals. Other metals may alter the chemical extraction process; therefore, controls on their abundance in the initial metal or the addition of process steps to eliminate their effects may be required. For example, aluminum or silicon may seriously affect melt refining by reducing TRU elements to metallic forms that are soluble in molten metals. It is possible that the effects of aluminum or silicon may be controlled by removing them prior to processing or by sparging the molten metal with air to oxidize the aluminum or silicon and the TRU elements.

In developing a process for a specific metal waste, it may be advantageous to perform additional experiments directed at determining the effects of known contaminant metals as well as procedures for minimizing their detrimental effects.

In the experimental program, the melt-refining process was not sensitive to the composition of the slag. Therefore, the slag composition need not be specified in the design criteria. Slags may be obtained from commercial sources or may be prepared from metal oxides. Alternatively, the slag may be selected from a TRU waste stream. For example, glass from labware (bottles, beakers, etc.) or from process equipment (condensers, tubing) that is contaminated with plutonium or americium may be a useful slag.

The composition of the slag is expected to affect the rate of corrosion of the oxide crucible and hence the length of time the crucible will remain in service. Therefore, it may be advantageous to prepare slags of

specific compositions from chemical stock rather than to use glass or other metal oxide wastes of unspecified compositions.

Slags high in alumina content, such as those composed of nepheline ($(K, Na)AlSiO_4$) or alkali feldspar ($(K, Na)AlSi_3O_8$), may be compatible with an alumina crucible. Solutions of nepheline or feldspar have eutectic temperatures considerably below the melting points of ferrous metals and, therefore, are suitable as slags.

Alternatively, a slag composition could be selected that may be in equilibrium with alumina at the temperature at which the metal is held molten. Anorthite ($CaAl_2Si_2O_8$), the calcium feldspar with about 5% Al_2O_3 exists as a liquid at $1550^\circ C$ in equilibrium with alumina.

The amount of extraneous material (that is, nonmetals oxides) that could be tolerated in the metal or slag used in processing would depend on the properties of the material. Organic materials in the form of paints, oils, plastics, etc. are likely to be the major extraneous materials. These materials are combustible and in the presence of oxygen would form gases and fumes during the melt process. In the absence of oxygen, these materials may form carbides or reduce the TRU-element oxides, thereby interfering with the melt-refining process.

Another possibility is that extraneous material may be in the form of halides or other salts that could interfere with the melt-refining process. Generally, the amount of extraneous materials should be kept low--possibly below 2% of the weight of the metal. It is assumed for the process criteria that (1) the metals can be sorted to reduce extraneous material to this level and, (2) at the 2% level, the extraneous material does not interfere with the melt-refining process.

2. Process Capacity

For the design criteria, processing facilities of two sizes have been considered. For a pilot-plant scale facility (smaller-size facility) furnace and crucible capacities to melt and contain 40 kg of metal and 4 kg of slag were adopted. A larger facility was also considered in which up to 150 kg of metal and 15 kg of slag could be handled in the furnace and crucible.

These facilities are larger by factors of 20 and 75 respectively, than the laboratory facility. The two facilities and their process designs are similar. Essentially only in aspects related to scale of operation, which determines portability, type of support facilities, etc., are the two designs dissimilar. Therefore, the process steps which are described in Subsection C of this section apply to both facilities.

3. Characteristics of Process Product

The process is designed to produce a consolidated metal having no loose particles with activity on them and a concentration of TRU elements whose combined activity is below 10 nCi/g of metal. Under proposed federal regulations, material meeting this design criteria may be disposed of in commercial burial facilities and need not be stored in a retrievable fashion. The metal product must be assayed to determine that its TRU element level is below the 10 nCi/g limit. No provisions are made in the conceptual design to remove from the metals radionuclides other than those of plutonium and americium.

The primary waste stream from the process is designed to contain the TRU elements in as concentrated a form as possible and to maintain a low contamination level of the metal product. The TRU elements should be confined in the waste material in a way to minimize handling difficulty. Additional concentration of the TRU elements in the waste or recovery of the TRU elements may be possible, but no provisions have been made to treat the TRU elements further in the processing scheme. An additional objective is to minimize the quantity of secondary waste streams such as aqueous washes, crucible material, and abrasive compounds that may result from additional treatments of the process material.

C. Process Steps

To achieve the objectives of the process plant, the conceptual design was formulated utilizing batch processing rather than continuous processing. The conceptual design can therefore be described as a series of steps whereby a batch of material would be transformed into the desired products. These steps include the initial treatment of the metal (sorting, size reduction), melt refining (melting, pouring) and subsequent assaying of the metal product.

1. Sorting

In the conceptual design, the TRU-contaminated metal wastes are handled in a sorting area, where ferrous and nickel metals are separated from other materials. The other materials may consist of parts of shipping containers (e.g. plastic containers, wood crates, etc.) or be parts of the items being disposed of (e.g., Bakelite terminal boards, copper motor armatures, etc.).

Because beta-gamma emitting radionuclides are absent, the sorting can be performed manually in a glove box facility. The initial sorting may be by hand to remove large objects such as boards or plastic bags that would interfere with additional sorting procedures. Hand-tools such as wrenches and saws can be used to remove undesirable materials that are attached to metals.

Wiping or washing operations can be employed to remove visible masses of plutonium or americium, oils, etc. The amount of metal to be processed for each 8 h of plant operation is about 80 kg for the pilot plant and 150 kg for the large-scale unit.

Depending on the characteristics of the metals, automatic sorting procedures to treat this mass of material may be desirable. For example, after shredding of wastes in preparation for incineration, metal wastes are separated from combustible wastes.²⁹ The metal pieces from such operations are likely to be small and uniform in size. This noncombustible waste can be sorted automatically by magnetic property and density to form a waste product suitable for melt refining. First, the magnetic metals (ferrous steels and nickel) can be separated from the nonmagnetic materials. Secondly, a density separation can be used to separate stainless steels from lighter metals such as aluminum and from most combustible materials. Metals such as brass or copper would separate with the stainless steel, and 5% of the total weight could consist of such metals.

Material that is not suitable for melt refining and is rejected in the sorting would constitute the initial waste stream from the melt-refining process. Much of this would be combustible material suitable for incineration. Metals such as aluminum may be treated by another method--for example, by oxidation and glassification. Therefore, it may be desirable to separate this waste for further treatment before it is removed from the sorting area.

2. Size Reduction

In this operation, the size of metal waste objects is reduced so that the waste can be handled in the loading and batching operation of the melt-refining process. Size reduction, along with further loading after partial melting of the metal, would permit crucibles to be loaded with metal to 60% of their total volume.

The metal pieces must be small enough to fit into a furnace crucible. The inner dimensions of the crucible thus limit the maximum dimensions of a metal piece. For the pilot plant, crucibles of 20-cm ID and 25-cm height are envisioned. For the large-scale plant, crucibles of 33-cm ID and 35-cm height would be used. Generally, for material with voids such as tubing or convoluted metals, it is desired that individual pieces be significantly smaller than the crucible dimensions--perhaps by a factor of 4 or more.

The proximity of the operators to the materials allows a variety of devices to be used for size reduction. Hand tools such as wrenches or mechanical saws may be used. Other means of size reduction such as gas torches or electric arcs for cutting may be employed, but these may have the disadvantages of generating off-gases or dispersing radioactive material.

Recently, success has been reported³⁰ on the use of an arc saw for disassembling radioactively contaminated vessels. The saw utilizes a fast-response power supply that can adjust to variations in stand-off distance between the blade and the cut material. With this saw, cutting speed up to about 30 cm²/s at depths as great as 45 cm are possible. For certain materials such as sheet metal, shears or compactors may be suitable for size reduction.

3. Melting

After sorting and sizing operations, the metal waste is ready for refining and is loaded into the crucible along with slag weighing 10% of the metal weight. A tilt and bottom pour crucible is to be used in the pilot plant operation. Because of size considerations, the crucible in the large-scale plant is limited to bottom-pour capability. Both crucibles are loaded from above, with initial loading of cold materials but with loading continued during melting to provide 60% loading of the crucible.

The metal and slag are maintained molten for one hour. The solution is stirred for 45 minutes and allowed to settle for 15 minutes. Before the metal is poured a sample of the slag is obtained for analysis to determine its plutonium concentration. This is done from the top of the melt by dipping with a small ceramic ladle or hoop. This sample is cooled and assayed prior to tapping the metal. If the plutonium content of the slag exceeds 3.5 mCi/g in the pilot plant, or 0.9 mCi/g in the full-scale plant, the slag will be poured from the crucible after casting of the metal. Otherwise, the slag will remain in the crucible for the next melt-refining run.

The 3.5- and 0.9-mCi/g limits for the pilot plant and the full-scale plant, respectively, for TRU content of the slag were selected based on extraction properties of the slag, on operating considerations, and on considerations of criticality. Slags containing 11% plutonium (10 mCi/g) were found to be associated with metals that had been effectively decontaminated to below the 10-nCi/g level (which is the lower limit for TRU-contaminated waste).

In the experimental program, no chemical fractionation of americium from plutonium was seen. The decontamination of other TRU elements may be considered to be similar to that of plutonium.

4. Metal Casting

The molten metal is tapped from a bottom hole in the crucible. A sample of the molten metal stream is taken in a ladle before the metal reaches the mold. The metal sample is cooled to form a disc for radiochemical analysis. If necessary, an additional sample is taken and stored to serve as a retrievable aliquot of the processed metal.

The fraction of the steel that may be tapped from the crucible is limited by the requirement that no slag drain with the metal. It was assumed that 80% of the metal can be poured without slag leaving the crucible. After a metal ingot cools, it is surveyed for surface alpha activity. The ingot is then imaged by ultrasonic techniques to verify that there are no voids or slag inclusions in the ingot. Any metal ingots suspected of containing TRU contamination in excess of 10 mCi/g metal may be recycled.

The maximum size of metal ingots is limited by the possibility that an ingot will have to be recycled. Therefore, two ingots are poured from each batch. Thus, an ingot that contains an internal defect may be recycled without further size reduction being needed. Melt refining may now be repeated with scrap or recycled metal, provided the TRU-element content of the slag is below 10 mCi/g for the pilot plant and below 3.5 mCi/g for the large-scale plant. When TRU-element concentration exceeds these values, the slag is poured out of the crucible.

5. Slag Pouring

When the TRU-element content of the slag is found to exceed 10 mCi/g for the pilot plant or 3.5 mCi/g for the large-scale plant, the slag is removed from the crucible. In pilot plant operations, the slag is poured by tilting the furnace and the slag is cast into glass forms. In large-scale operation, the slag is removed by bottom pouring after the metal and slag in the metal-slag boundary layer have been poured. The latter mixture of metal and slag can be recycled if it is largely metal or discarded with the slag if it is largely slag.

6. Process Capacities

In Table 8, the conceptual process steps for a melt-refining facility are summarized. The design data for the pilot plant and large-scale facility are given in Table 9. Although the plants are for basically the same operations, their difference in size necessitates differences in plant construction. The pilot plant is to be built in modules that would be transportable. The modules would operate at a site for as long as necessary to process the metal scrap in that locale and then would be transported to another location to process metal scrap at that site. The larger plant would be built as a stationary facility. Metal waste would have to be transported to the facility, and the processed materials then transported for permanent storage. The larger facility would have the advantage in comparison to the portable unit of being able to run continuously with permanent support capabilities (work force, utilities, etc.).

In Table 10 the design output of the two plants is shown. The furnace utilization factors (crucible loading and metal tapping efficiencies) were estimated consistent with process requirements. The crucible-loading

Table 8. Conceptual Process Steps for a Melt-Refining Plant

Conceptual Process Step	Design Specification
Sorting	Ferrous, nickel, and chrome metals containing less than 5% other metals and less than 2% combustible materials.
Scrap Size Reduction	Size reduction of scrap allows the scrap to be loaded into a furnace crucible.
Crucible Loading	Metal-slag mixture in the ratio 10:1 by weight. Load the crucible to 60% of its maximum volume.
Melting and Slagging	Molten system stirred for 45 min. and allowed to settle for 15 min.
Slag Sampling	A slag sample is ladled from the top of the melt for analyses.
Metal Casting and Sampling	Bottom-tap two ingots without slag admixture. A sample of the molten metal is taken with a ladle at the bottom tap.
Ingot analysis	Measure the alpha activity of the ingot surface and alpha activity of metal sample. If it is greater than 10 nCi/g, recycle the ingot.
Slag analysis	Remove the slag from the crucible if its concentration exceeds 10 mCi/g in the pilot plant or exceeds 3.5 mCi/g in the full-scale plant.

efficiency is limited by the amount of time required for loading, and the amount of metal that can be tapped from the crucible is limited by the requirement that no slag be removed with the metal. Batch time requirements were estimated. They allow a greater length of time for loading and melting of the charge in the large furnace and for removing the metal and slag. Although the large plant can handle nearly four times as much material per batch, the net output is only a factor of 2 larger than that of the pilot plant. The size of a plant is limited by considerations of criticality (as discussed in a following section).

Table 9. Design Data for the Pilot Plant and Large-Scale Plant

Facility	Pilot Plant	Large-Scale Plant
Transfer containers	5-gal drums	55-gal drums
Scrap Size Reduction	15 cm max dimension	25 cm max dimension
Furnace type	Induction	Electric-arc
Crucible size	20-cm ID 25-cm height	33-cm ID 35-cm height
Metal charge	40 kg	150 kg
Slag charge	4 kg	15 kg
Plant	Portable, three trailer units	Stationary
Plutonium content of the metal charge (400 ppm Pu)	16 g	60 g
Plutonium content of slag containing 4% Pu	160 g	--
Plutonium content of slag containing 1% Pu	--	150 g

D. Other Considerations1. Ventilation

Ventilation and off-gas treatment facilities must be provided to remove fumes generated during melting and slagging and to prevent radioactive gases or particulate matter from leaving the confinement. The ventilation system must also serve the other process areas such as the sorting and size-reduction areas.

Table 10. Design Output for the Pilot and Large-Scale Melt-Refining Plant

Factor	Pilot Plant	Large-Scale Plant
<u>Furnace Utilization</u>		
Crucible loading efficiency	60%	60%
Metal tapping efficiency	80%	80%
<u>Batch Time Requirements</u>		
Loading and Melting	30 min	90 min
Stirring	45 min	45 min
Settling	15 min	15 min
Tapping and Slagging	30 min	60 min
<hr/>		
Total Process Time	2 h	3 1/2 h
Batches in 8-h period	4	2
Output (8-h period)	77 kg	144 kg

To design the ventilation and off-gas treatment facilities, characteristics of the off-gases must be estimated. For a process material consisting of metal contaminated with plutonium or other TRU elements only, very little fuming would be expected during melting. The plutonium and americium are expected to be completely incorporated in the nonvolatile materials. Contaminants in the off-gas stream would exist mainly in particulate material entrained in the off-gas stream. The particulate material could be formed as a result of any gas bubbling through the slag. The entrainment could be reduced minimizing ventilation air flow, and the remaining particulate material could be controlled with baffles.

Fuming during melting could be a major problem if the feed material should contain significant quantities of organic materials such as paints or oils. The fumes would be expected to be proportional to the quantity of

organic material processed. Reduction of the organic content of the feed material is provided in the sorting and size reduction processes. Even in the presence of organic material, the plutonium or americium would be expected to remain in the condensed phases. However, the larger volume of gas (CO_2 , volatile organics) generated during melting would be expected to increase the amount of fine particulate material generated by gas bubbling through slag. The larger volume of gas may require increased ventilation for its control, with subsequently increased entrainment and transport of the particulate material.

If neutron-activation products are present in the feed material, the ventilation and off-gas treatment systems may be complicated. In principle, radionuclides of any of a number of elements could be present in the waste stream. Radionuclides of the elements hydrogen and carbon, for example, may be expected in the off-gas if they are present in the waste. Radionuclides of other elements such as tellurium and selenium would be expected to volatilize to some degree and might also be present in the off-gas. These elements may condense as fine particles or remain as gases during off-gas treatment. Radionuclides of metals such as iron, nickel, or chromium would be expected to remain with the molten metal. The design of ventilation and off-gas treatment facilities for handling non-TRU contaminants must be related to the characteristics of the off-gas stream. If these characteristics are not known prior to plant design, the plant design may provide for gas-stream sampling and analysis systems in the off-gas treatment facility.

2. Criticality and Safeguards

a. Criticality

At the scale of the proposed pilot plant and large-scale plant, conditions must be implemented that ensure there will be no reaction of fission events as a result of the assembly of neutron-fissionable material. In the proposed pilot plant, 4 kg of slag would be used with 40 kg of metal. At the concentration of 400 ppm plutonium considered typical of the metals to be processed, the amount of plutonium per batch would be 16 g. The amount of plutonium that would be allowed to accumulate in the slag is 3.5 mCi/g, corresponding to about 160 g in a batch of slag.

In the large-scale plant, 150 kg of metal would be processed in a batch, along with 15 kg of slag. The amount of plutonium in the contaminated metal in a batch would typically be 60 g, with 150 g plutonium allowed to accumulate in the slag. The plutonium concentration in the slag when it is discarded is lower than in the pilot plant because the amount of plutonium allowed in each discarded slag is the same.

The quantities of plutonium or other TRU elements that may accumulate in one cycle of the melt-refining process present no criticality hazard. However the massing of several slag charges of the size that may accumulate in the process would be of concern. This could occur, for example, on a slag heap. Provisions must be made to monitor the incoming metal waste to estimate its content of fissionable isotopes and to remove TRU-element-bearing materials from the process area, in so far as possible, before a chain reaction becomes a possibility.

b. Safeguards

The melt-refining process is a process of concentration in which TRU elements present in metals in low concentrations, are separated and enriched in the process slag. Because of this enrichment, the process slag is more attractive for diversion than is the original contaminated metal. Therefore, safeguards not necessary for the contaminated metal may have to be implemented for the process slag to ensure controlled handling. The processed metal, now low in TRU-element content, may be free of safeguards previously required.

3. Metal Product Characterization

a. Determination of Defect Locations

High concentrations of plutonium are associated with defects in processed metal ingots. A defect that formed on an internal surface of the metal ingot from experiment 126 is shown in Fig. 10. Although the defects are not abundant, they are a major source of the plutonium associated with the processed metal. Consequently, methods were examined for quickly scanning ingots in a nondestructive manner to locate similar defects. The metal containing the defect could then be treated appropriately.

Ultrasonic probing was found to be the most promising technique³¹ for locating defects. An ultrasonic imaging system (shown in Fig. 11) may be devised which includes a single piezoelectric transducer, an ultrasonic driver, and an oscilloscope. The transducer is shock-excited with a voltage spike, and the generated sound pulse is transmitted to the ingot. A difference in the acoustic impedance (mass density x sound velocity) caused by a defect gives rise to an echo which can be picked up by the same transducer, amplified, and viewed on the oscilloscope. For voids in metals, the impedance discontinuity is essentially infinite, giving a high sensitivity of ultrasound in defect detection. The location of the defect can be determined from the time of flight of the pulse and echo.

The sensitivity of ultrasonic imaging is directly related to the ultrasonic frequency and the nature of the defect being imaged. The smallest defect that can be detected is related to the frequency employed and is not

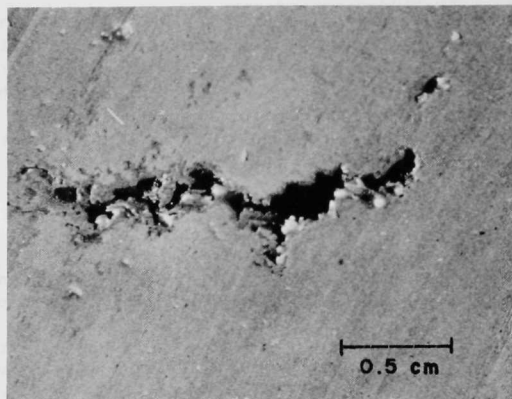


Fig. 10. Defect Consisting of Dark Metal Lining a Void in the Steel Ingot. Experiment 126. About one defect is found for every 0.01 m^2 of cut surface. The defects have significant amounts of plutonium associated with them and constitute a major source of plutonium in the ingot. Striations from upper right to lower left are saw marks.

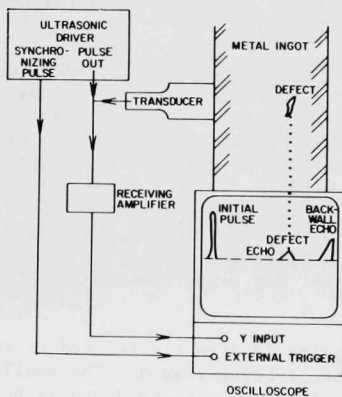


Fig. 11

Schematic of Ultrasonic Imaging System for Detecting and Locating Defects in Metal Ingots

limited by transducer size (as is resolution). For frequencies in the range, 2 to 20 MHz, voids in metals about the size of the sonic wavelength or larger can be detected (approximately 0.3 to 0.03 cm for compression waves and half this for shear waves over the stated frequency range). This sensitivity is more than adequate to detect defects in metal ingots. Yee and Couchman summarized ultrasonic examination principles and methods.³²

b. TRU Element Assay

The capability to analyze metals and slags for plutonium and americium at various points in the process is required. Assays of the waste metals are needed (1) to ensure that a chain reaction of fission events does not occur and (2) to manage the decontamination process. These assays are required for large quantities of plutonium or americium that generate sufficient radiation for counting by passive techniques. Similarly, analyses of slags to detect high levels of alpha activity (3 to 10 mCi/g of slag) may be performed by existing analytical techniques.

Processed metals having low levels (<10 nCi alpha activity per gram of processed metal) of alpha activity must be analyzed to establish whether or not they meet standards governing the activity levels of cleaned equipment. The generation of compact forms with homogeneous plutonium distributions in the metal matrix simplifies analysis considerably. Heterogeneities due to silicate slag adhering to the surface of the ingot or radionuclides at defects in the interior of the metal ingots may be reduced by appropriate process design or may be detected by surveys of the ingot surface or by ultrasonic imaging.

The radionuclide content of the processed metal may be assayed by established techniques, using equipment appropriate for the processed metal. Because the matrix of the metal contains a uniform distribution of radionuclides, the metal may be sampled at any location on the ingot. The analyses of the sample can either be nondestructive or be done by chemical dissolution and radiochemical counting.

Alternatively, nondestructive analyses (NDA) of large masses of the metal ingots may be performed by active or passive counting methods.²⁰ Because of the uniform shape of the metal product, the assay procedures may be calibrated for various concentrations and types of radionuclides. The NDA methods that may be used for low levels of TRU elements include principally passive gamma counting, passive neutron counting, active neutron counting, and active gamma counting. These methods have been used successfully as analytical tools in routine operations in the nuclear industry.

With appropriate calibrations, low levels of plutonium concentrations may be detected by counting low-energy electromagnetic radiations (17-keV L X-rays and 60 keV gamma rays).

Coincidence neutron counting, whereby neutrons from spontaneous fissions are detected, has been successfully employed for assaying ^{240}Pu . Neutrons are insensitive to matrix materials that do not contain low-Z elements; hence, neutron counting is a potentially useful tool in assaying the large masses of processed metals. Because of the standard shapes of the metal ingots, design of high-efficiency detectors for use in coincidence neutron counting is possible.

In active neutron assays, neutron sources are used to produce fission of radionuclides in the sample. Delayed neutrons are detected. The method is applicable to fissionable isotopes and may be used for assaying total fissionable content for inventory management and waste sorting. Although the active neutron assay is a proven analytical tool, it currently has only modest sensitivity. The limit to sensitivity and the elaborate equipment required for measurements make this method less desirable than other methods for assaying fissionable elements in the processed metal.

The active gamma assay method uses the measurement of prompt gamma rays emitted following the fissioning of a nuclide after neutron capture. The prompt gamma energies are high for ^{239}Pu (50 to 6.5 Mev). Thus, the method may be useful for analyzing massive ingots of processed metal.

In summary, both destructive (sampling and analyses) and non-destructive analytical methods are feasible for use on the processed metal. The design of high-efficiency detectors and the calibration of counting systems is considerably simplified because the product metal is homogeneous in TRU element content and the metal ingots are of standard shape.

E. Conclusions

A conceptual design of a process that utilizes the strong fractionation of plutonium and americium from contaminated metals to silicate slags is presented. The process includes single-stage refining of contaminated metal to produce a metal product containing less than 10 nCi/g of TRU element contamination. The plutonium or other TRU elements separated from the metal are concentrated in a silicate slag. The final concentrations of TRU elements allowed in the slag are limited by considerations of criticality, rather than by its effect on the TRU element concentrations in the process metal. Two conceptual plants are described. A small one may be portable. The larger one is stationary and may be near the maximum size practical for a metal decontamination process that concentrates TRU elements in slag.

APPENDIX

Counting Data

The counting data obtained in the analyses of metals and slags obtained from the experimental program are given in this appendix. These data were used to calculate concentrations of plutonium and americium which are given in the appendix and in the main body of the text.

Table A-1. Counting Data from Alpha Tracks of Metals as Recorded in Cellulose Nitrate Detectors

Sample	Cellulose Nitrate, hours exposed	Number of Tracks Counted	Fields of View	Magnification ^a	Alpha-Track Density $\delta_{\alpha, \text{Pu}}$	Calculated Concentration of Plutonium, ^b C_{Pu} , ppm
53(mid-top)	145	0 ^c ,d	10	43x	10.0	<0.0004
73(mid-top)	143	0 ^c	10	43x	10.2	<0.0004
76(mid-top)	143	0 ^c ,d	10	43x	10.2	<0.0004
		hot spots				
78(mid-top)	143	0 ^c	10	43x	10.2	<0.0004
80(mid-top)	96	0 ^c ,0 ^c	40	43x	15.2	<0.0005
82(mid-top)	168	0 ^c	10	43x	8.7	<0.0005
107(top)	168	195	35	43x	48.3	0.0018
107(mid-top)	168	20	10	43x	8.6	0.0006
107(middle)	288	206	40	43x	26.1	0.0010
107(bottom)	168	48	15	43x	27.7	0.0010
109(top)	254	25	28	43x	5.1	0.00019
109(mid-top)	254	4	10	43x	2.3	0.000089
109(middle)	254	19	22	43x	4.9	0.00019
109(mid-bottom)	254	47	17	43x	15.8	0.00062
109(bottom)	254	12	16	43x	4.3	0.00017
111(top)	254	122	15	43x	46.6	0.00180
111(mid-top)	254	144	14	43x	58.9	0.00227
111(middle)	254	130	18	43x	41.3	0.00159
111(mid-bottom)	254	131	10	43x	75.0	0.00289
113(top)	254	1	23	43x	0.25	0.0000096
113(mid-top)	254	1	22	43x	0.26	0.000010
113(middle)	254	6	40	43x	0.859	0.000033
113(mid-bottom)	254	3	15	43x	1.1	0.00004
113(bottom)	254	1	26	43x	0.22	0.000009
113(bottom)	254	5	12	43x	2.4	0.00009
115(top)	254	2	14	43x	0.82	0.00003
115(mid-top)	254	1	10	43x	0.58	0.000022
115(middle)	254	2	11	43x	1.04	0.00004
115(mid-bottom)	254	9	30	43x	1.72	0.00006
115(bottom)	254	12	33	43x	2.08	0.00008
117(top)	312	317	10	96x	762	0.0293
117(mid-top)	312	47	1	96x	1129	0.0434
117(bottom)	312	426	9	96x	1136	0.0438
119(top)	66.8	32	9	43x	77.4	0.0030
119(top)	622	65	8	43x	19.0	0.0008
121-1(avg.)	114.3	28	20	43x	17.8	0.0006
121-2(avg.)	114.3	233	18	43x	164	0.0063
121-3(avg.)	694	861	19	96x	489	0.0186
124-1(avg.)	694	328	36	96x	98.4	0.0037
124-2(avg.)	694	699	18	96x	419	0.0162
126(middle)	958	160	5	43x	48.5	0.0019
126(end)	958	33	4	43x	12.5	0.0005
126(end)	958	22	2	43x	16.7	0.0006
126(avg.)	958	215	11	43x	29.7	0.0012

(contd)

Table A-1 (contd)

Sample	Cellulose Nitrate, hours exposed	Number of tracks Counted	Fields of View	Magnification ^a	Alpha-Track Density $\delta_{a,Pu}$	Calculated Concentration of Plutonium ^b , C_{Pu} , ppm
129(mid-top)	142	251	8	97x	166	0.0637
130-1(top)	1008	59	10	43x	8.5	0.00032
130-2(top)	1008	63	16	43x	5.7	0.00022
133(avg.)	1963	283	8	43x	26.2	0.0010
135(top)	1968	181	13	43x	10.3	0.00038
135(mid-top)	1968	116	14	43x	6.1	0.00024
135(mid)	1968	83	12	43x	5.1	0.00019
135(mid-bot)	1968	119	15	43x	5.9	0.00022
135(bottom)	1968	94	12	43x	5.8	0.00022
137(top)	557	182	12	43x	39.7	0.0015
137(mid-top)	557	148	12	43x	32.2	0.00123
139(top)	557	143	10	43x	37.4	0.0014
139(mid-top)	557	113	10	43x	29.5	0.00113
141(top)	1963	274	17	43x	11.9	0.00046
141(mid-top)	1963	150	11	43x	10.1	0.00038
143(top)	1968	282	11	43x	19.0	0.00072
143(mid-top)	1968	194	12	43x	11.9	0.00046
145(top)	557	324	1	43x	846	0.032
145(mid-top)	557	400	2	96x	2684	0.103

^aMagnification: at 43x, field of view is 0.0266 cm in diameter, Area = $\pi r^2 = 5.56 \times 10^{-4}$ cm²; at 96x, field of view is 0.0117 cm in diameter, Area = $\pi r^2 = 1.08 \times 10^{-4}$ cm².

^bConcentration, C_{Pu} , was calculated from the equation:

$$C_{Pu} = \frac{\delta_{a,Pu} \times 4}{(1.181 \times 10^{13}) (8.88 \times 10^{-3})}$$

where $\delta_{a,Pu}$ is the track production rate (tracks/cm²·h) due to alpha particles from the decay of plutonium. The track production rate $\delta_{a,Pu}$ was calculated from the alpha-track density measured in the plastic divided by the exposure time of the plastic and multiplied by the fraction of alpha particles from the decay of plutonium (0.809). The value, 1.181×10^{13} d/s·g, is the specific activity of plutonium in the oxide; the constant, 8.88×10^{-3} /cm², is the average range of alpha particles in iron.

^cThe limit of detectability was assumed to be one track per field of view in these initial measurements. During examinations of other plastics, track densities below 1 track/field were readily detected and measured, and thus the calculated concentrations of plutonium are considered only upper limits to the actual concentration.

^dSample 53 contained a few clusters of alpha tracks from plutonium particles. Excluding these clusters, no tracks representative of plutonium within the matrix of the metal were detected in ten fields of view.

^eThe slag from the arc-melting experiment was mushroom-cap shaped and the cross section was crescent shaped. The sample positions refer to the middle and two ends of the crescent-shaped cross section.

Table A-2. Fission-Track Counting Data for Neutron-Irradiated Samples

Sample	Sample Position	Neutron Irradiation ^a	No. of Tracks	Fields of View	Magnification ^b	Track Density, δ	Plutonium Concentration, ppm
<u>Metal</u>							
101	top	A	633	30	43	3.49×10^4	0.0018
109	top	B	404	9	43	8.07×10^4	0.00049
113	top	A	14	6	43	4.20×10^3	0.0002
113	top ^c	A	168	13	97	1.2×10^5	0.0055
113	top	B	154	7	43	3.96×10^4	0.00024
113	top	C	92	73	43	2.27×10^3	0.00013
115	top	A	77	8	97	8.92×10^4	0.0041
115	top	C	129	26	43	8.93×10^3	0.0005
115	top	C	107	26	43	7.40×10^3	0.0004
126	Avg	E	12	18	43	1.35×10^3	0.00007
Blank	Metal	A	--	--	--	1.80×10^{2d}	0.000008
<u>Epoxy</u>							
113	mount ^e	C	3	10	43	5.40×10^2	0.00003
115	mount ^e	A	50	4	97	1.16×10^5	0.0054
Blank	mount ^e	A	1	10	43	1.80×10^{2d}	0.000008
<u>Glass</u>							
126	Adjacent to Metal	C	175	1	97	1.62×10^6	0.090
126	Avg	C	251	12	97	1.94×10^5	0.0011
<u>Glass Standard</u>							
Standard		A	481 ^f	1	59.8	1.69×10^6	
Standard		B	174 ^f	1	59.8 ^e	1.28×10^7	
Standard		C	150	1	97	1.39×10^6	

^aNeutron doses were calculated for the irradiations, using the measured track densities from the standard glass to be 8.1×10^{19} , 6.1×10^{20} , and 6.6×10^{19} neutrons/m² for the three irradiations A, B, and C, respectively.

^bAt a magnification of 43, the field of view was 0.0266 cm in diameter and corresponded to an area of 5.56×10^{-4} cm². At a magnification of 97, the field of view was 0.0117 cm in diameter with an area of 1.08×10^{-4} cm².

^cTrack count was taken from a region having a high-track density from cross-contamination as evidenced by a similarly high track density in the mica adjacent to the epoxy.

^dIn scanning through many fields of view with the microscope, the track densities from the epoxy and from the uncontaminated mild steel were found to be comparable, as would be expected if the fission tracks originated from fissionable material (uranium) in the detector itself. Therefore, the track density from the epoxy was used to calculate an upper limit to the apparent plutonium concentration of the mild steel used in the experiments.

^eThe data are for the epoxy in the mount of the metal sample for which data are presented. The experiment number plus the neutron-irradiation can be used to correlate the data on the metal samples with data from the epoxy adjacent to the metal.

^fThese tracks were counted from photographs of 59.8x magnification. All other tracks were counted directly in a microscope.

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